

First deployment of an aerosol collection/thermal-desorption PTR-ITMS instrument for the *in situ* measurement of ambient aerosol organic species

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INTRODUCTION

Organic material has been observed to comprise a significant fraction of aerosol mass in many regions of the troposphere, but detailed measurements of the individual species that comprise the organic fraction have been limited in spatial extent and temporal resolution. Knowledge of the organic species present in atmospheric aerosols is needed to understand their effect on aerosol microphysical and optical properties as well as to resolve outstanding questions about important organic aerosol sources and formation mechanisms, and to elucidate the role of aerosols in the chemistry of the atmosphere through their interaction with gas-phase compounds. The measurement of aerosol organic compounds poses a significant experimental challenge due to the complexity and large number of organic species, and the low concentration at which individual species are present. The proton-transfer-reaction mass spectrometry (PTR-MS) technique has proved to be a useful tool in the study of atmospherically important volatile organic compounds (VOCs). Its ability to sensitively detect and quantify the concentrations of many common VOCs has led to an increased understanding of the sources, transport, chemical transformations, and loss processes of these compounds through both laboratory and field experiments. A logical extension of the technique is application to semi-volatile and condensed-phase organic species in the atmosphere. A new instrument that utilizes the PTR-MS technique to probe the organic composition of atmospheric aerosols has been developed. Aerosols are collected by impaction and then thermally desorbed into a carrier gas that transports the organic analyte molecules into a drift tube where they are ionized by reaction with H_3O^+ ions. Analyte ions are detected using an ion trap mass spectrometer. The instrument was deployed for the first time during summer 2006 in the Texas Air Quality Study aboard NOAA R/V. *Ronald H. Brown*.

THE INSTRUMENT

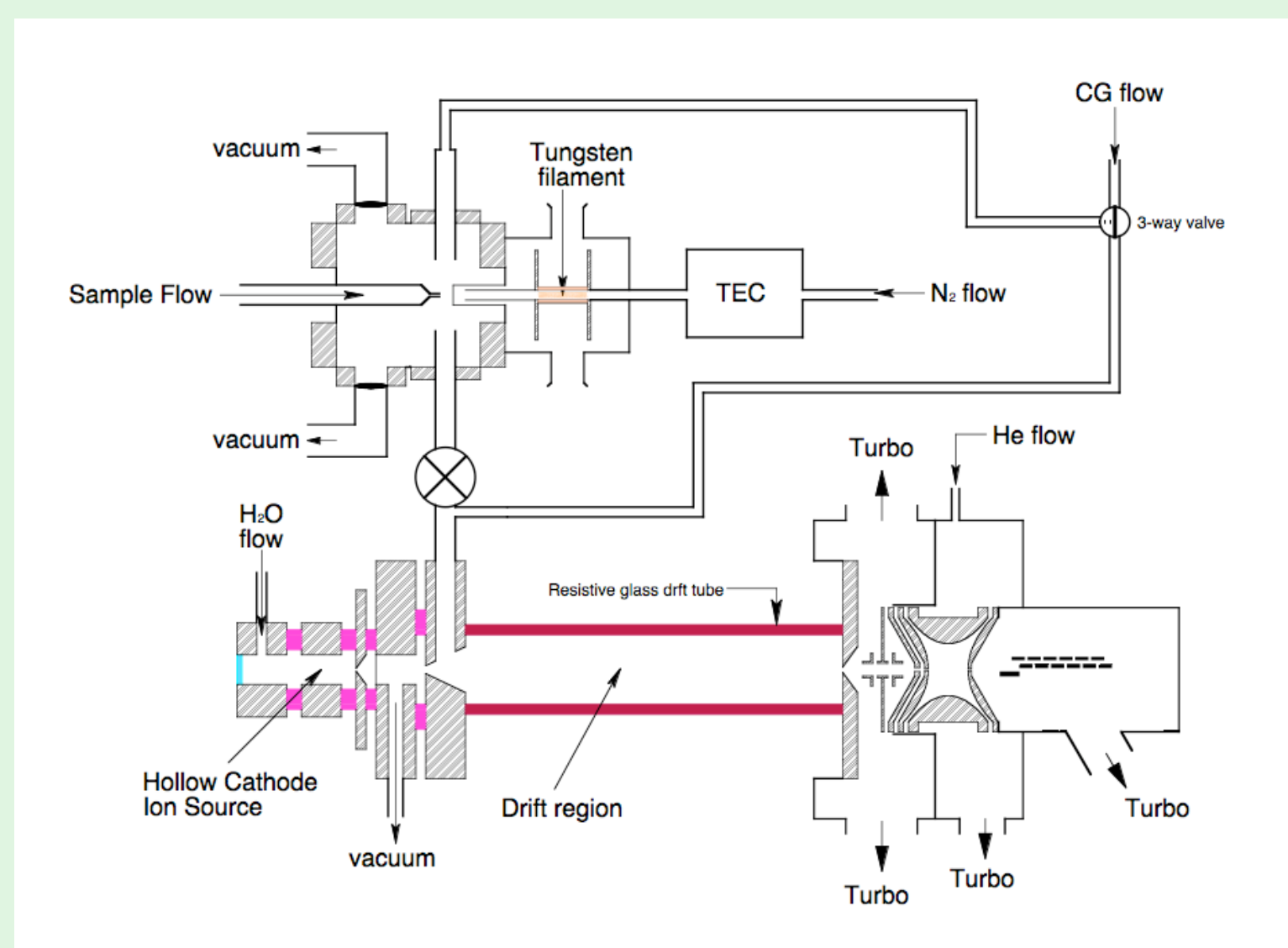


Figure 1: Schematic of the AOS-PTR-ITMS instrument

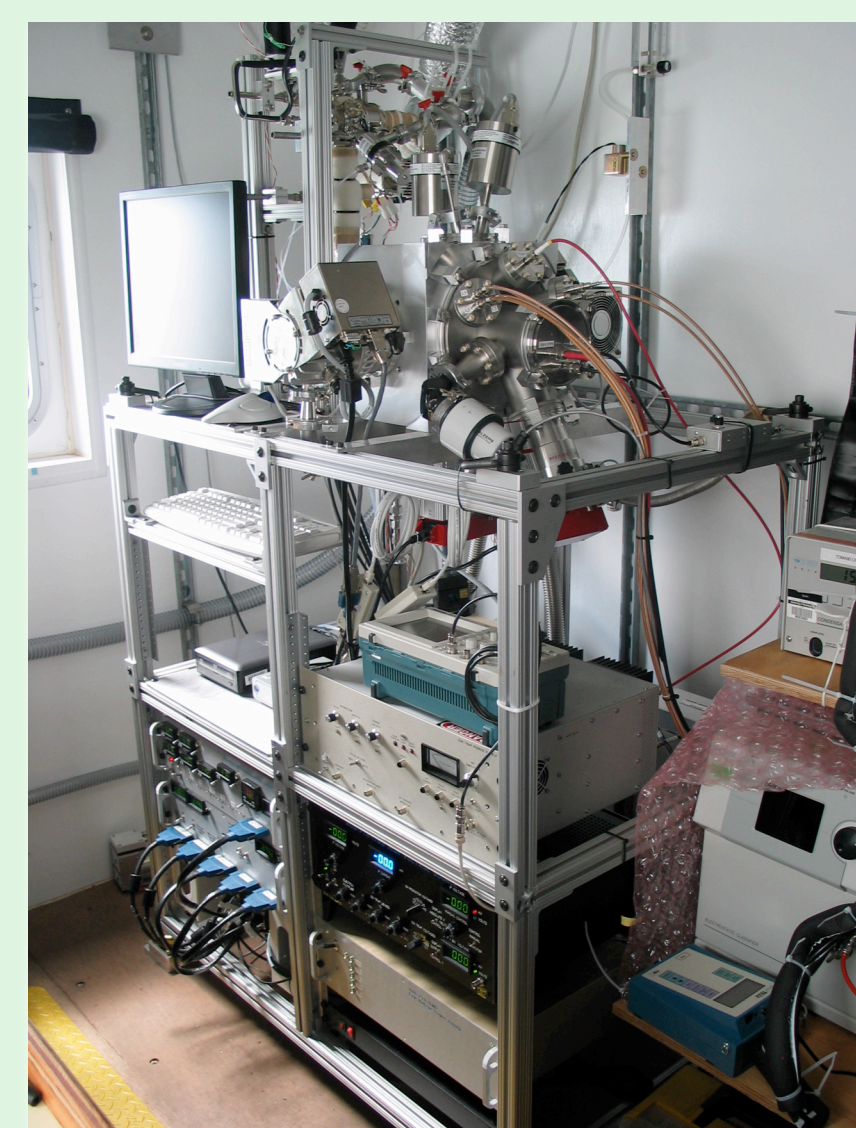


Figure 2: photo of instrument installed aboard NOAA R/V *Ronald H. Brown*

A schematic of the recently developed aerosol organic speciation instrument is shown in Figure 1. The instrument is composed of two principal components: an aerosol collection/desorption inlet chamber and a custom proton-transfer-reaction (PTR) ion trap mass spectrometer (ITMS). In order to reach a desired sensitivity for individual organic species in the low $ng\ m^{-3}$ range, aerosol collection was used to concentrate aerosol mass for analysis. Aerosol collection was accomplished by direct impaction of aerosols in a ~ 1.5 liter per minute (lpm) sample flow onto a cooled target. The aerosol inlet chamber, transfer line, and drift tube were all heated to $> 135^\circ C$ to reduce adsorption of desorbed compounds. The aerosol target was cooled to ambient/sub-ambient temperature by flowing 5 lpm nitrogen gas that had been passed through a thermoelectric cooler against the reverse side of the target. To desorb the organic material collected on the aerosol target, the temperature of the target was rapidly raised (~ 10 sec) to 150 - $160^\circ C$ by heating the nitrogen stream resistively with a tungsten coil. The efficiency of the aerosol collection as a function of aerosol diameter is dependent on the nozzle geometry. During the TexAQs study, the nozzle used was circular with a diameter of 0.5 mm. This led to a small size cut-point greater than 500 nm. The presence of an upstream $1\ \mu m$ cut-point impactor meant that the sampled aerosol size range was only $>0.5 - 1\ \mu m$. The PTR-ITMS instrument developed here is similar to the ion trap based PIT-MS instrument that was used to measure gas-phase organic compounds aboard NOAA R/V *Ronald H. Brown* during TexAQs (see Welsh-Bon et al. poster), with several modifications. The drift tube used was a single piece resistive lead glass tube (Burle Electro-Optics, Inc., Sturbridge, MA, USA), 25 cm long with an ID of 2.35 cm. The increased length required a higher voltage be applied to the inlet end of the drift tube in order to achieve declustering of ions, however the increased voltage required was significantly reduced when the drift tube was heated. The use of an ion trap as the mass spectrometric analyzer was dictated by the goal of continuously measuring the entire mass spectrum (high duty cycle at all masses) while desorbing the analytes rapidly in order to maximize the concentration in the carrier gas and shorten the sampling/analysis cycle time. The upper limit of the ion trap mass scan was 367 Thomson. During TexAQs, the instrument was operated on an alternating cycle of one ten-minute ambient sample and one five-minute background sample with the sample valve closed. The need for the frequent background determinations was motivated by high instrumental background signals arising from the presence of rubber seals in the heated inlet chamber, transfer line, and drift tube. The difference between sample and background conditions resulted in some masses having negative baselines. A photo of the instrument as it was installed in the PMEL#3 van on NOAA R/V *Ronald H. Brown* during 2006 TexAQs/GoMACCS is shown in Figure 2.

2006 TexAQs/GoMACCS Operating Parameters

- Sampled through PMEL aerosol mast with upstream $1\ \mu m$ (@60% RH) cut-point impactor
- ~ 12 m length of 1.5 cm ID stainless tubing, 30 liters per minute total flow
- 1.5 liter per minute sample flow
- Collected aerosol size range $>0.5 - 1\ \mu m$
- Aerosol target temp $\sim 27^\circ C$ during collection
- Alternated 10 minute sample (15 liters of air) and 5 minute background (no flow) runs
- Typically acquired and analyzed 44 samples per day

RESULTS I - Photochemical SOA

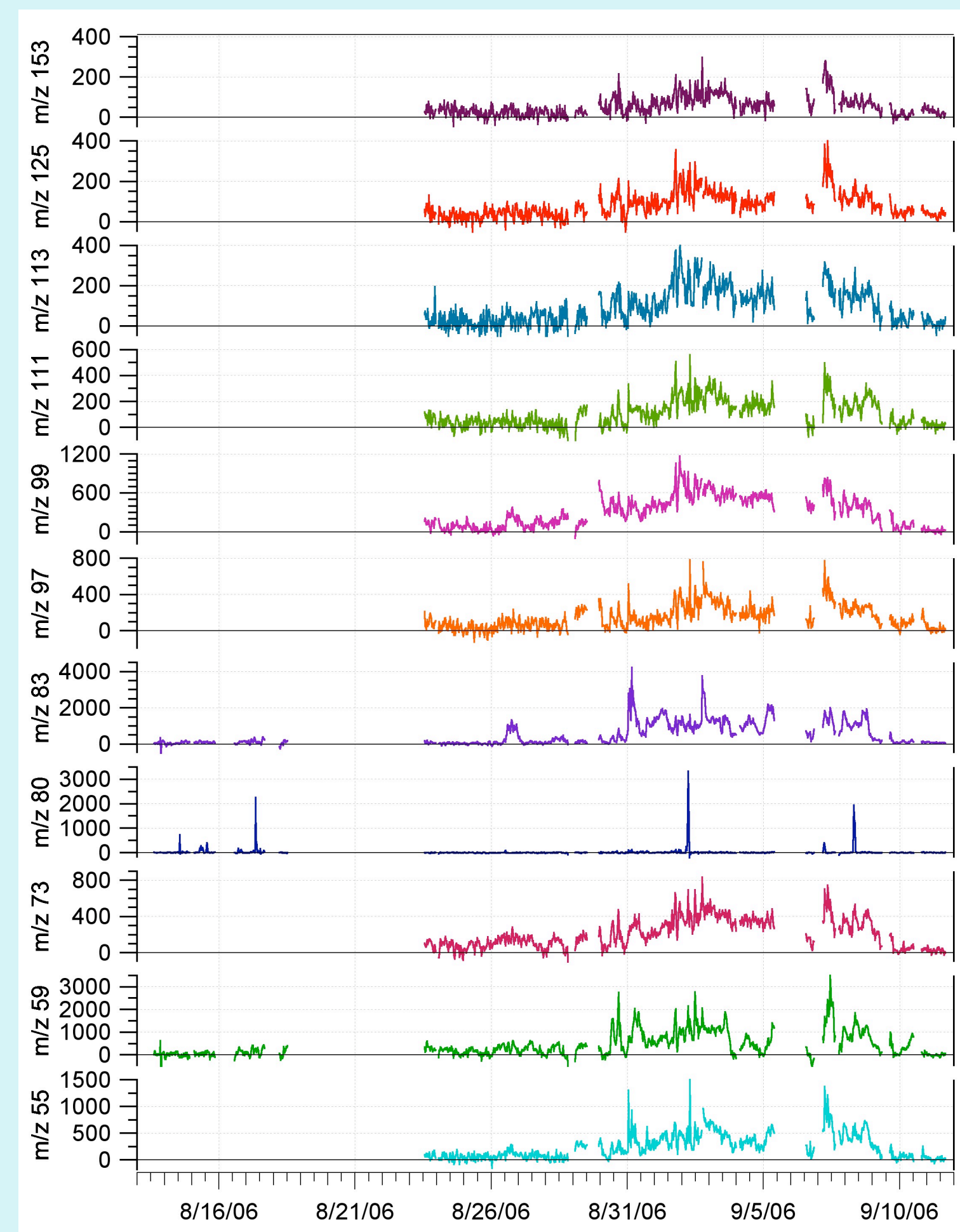


Figure 3: Time series of the signal (arbitrary units) observed at a number of masses.

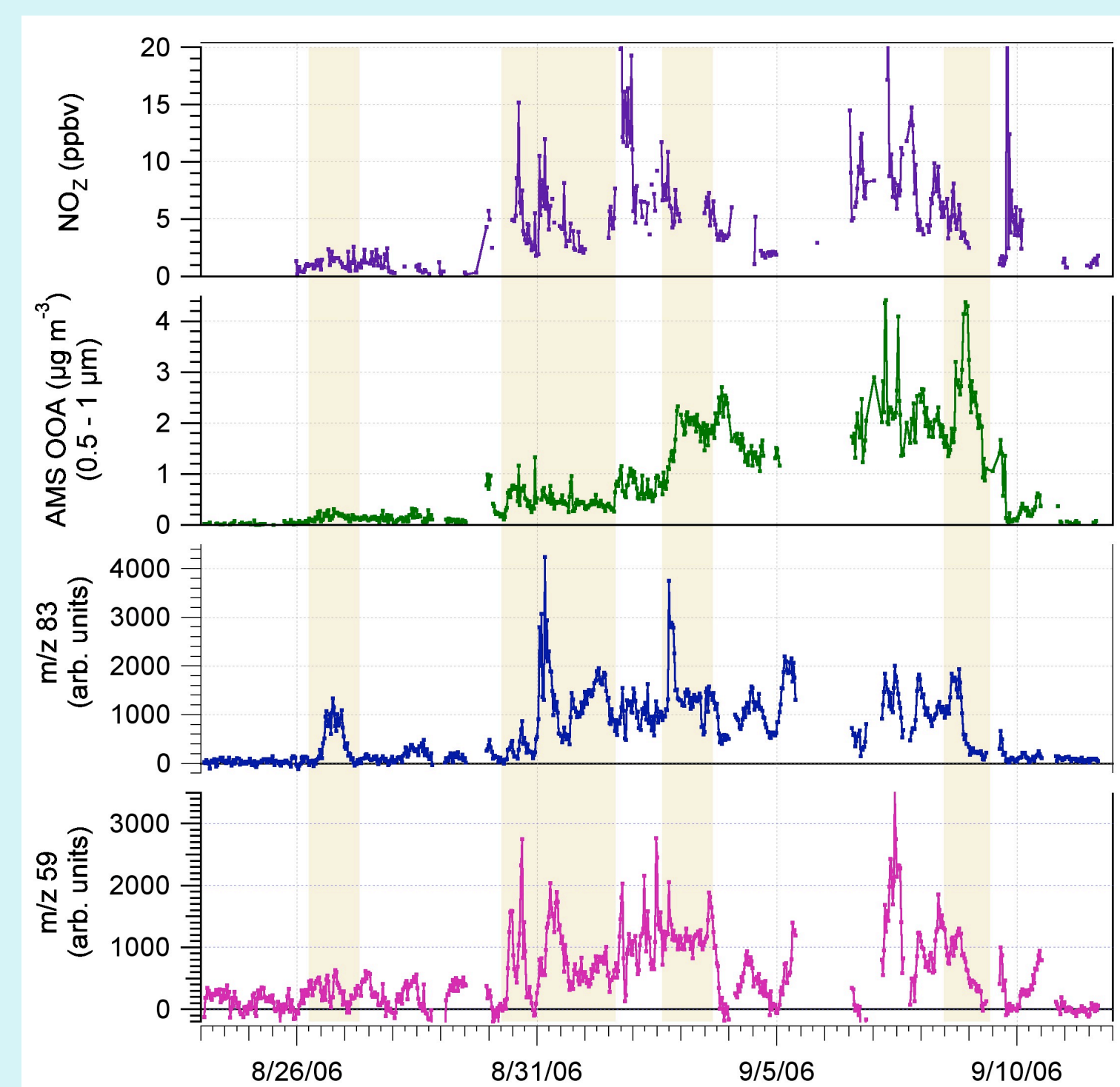


Figure 5: Time series of $m/z\ 59$ and $m/z\ 83$ along with PMEL AMS OOA (multiplied by submicron aerosol volume fraction $>0.5\ \mu m$) and NO_2 as a tracer of photochemical oxidation.

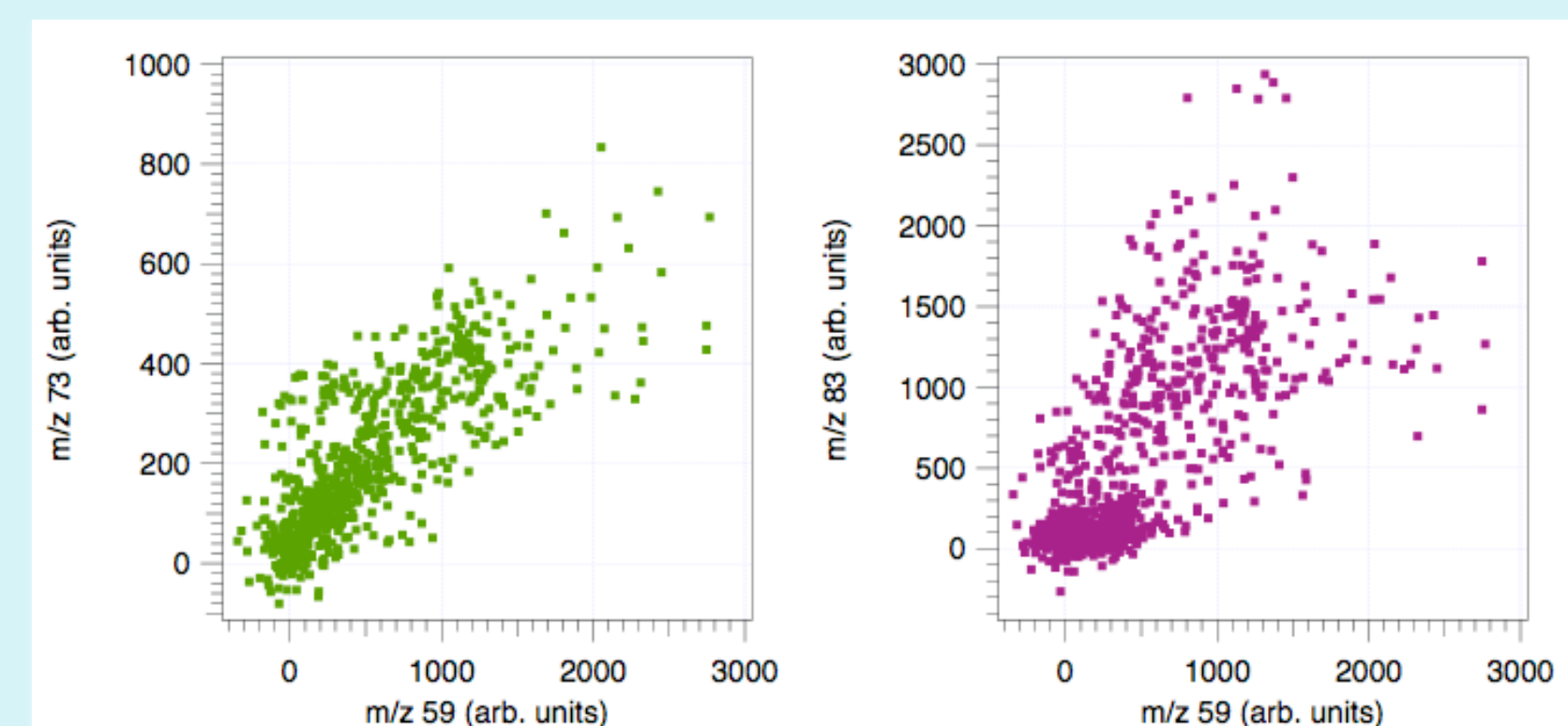


Figure 6: Observed correlation between different mass signals.

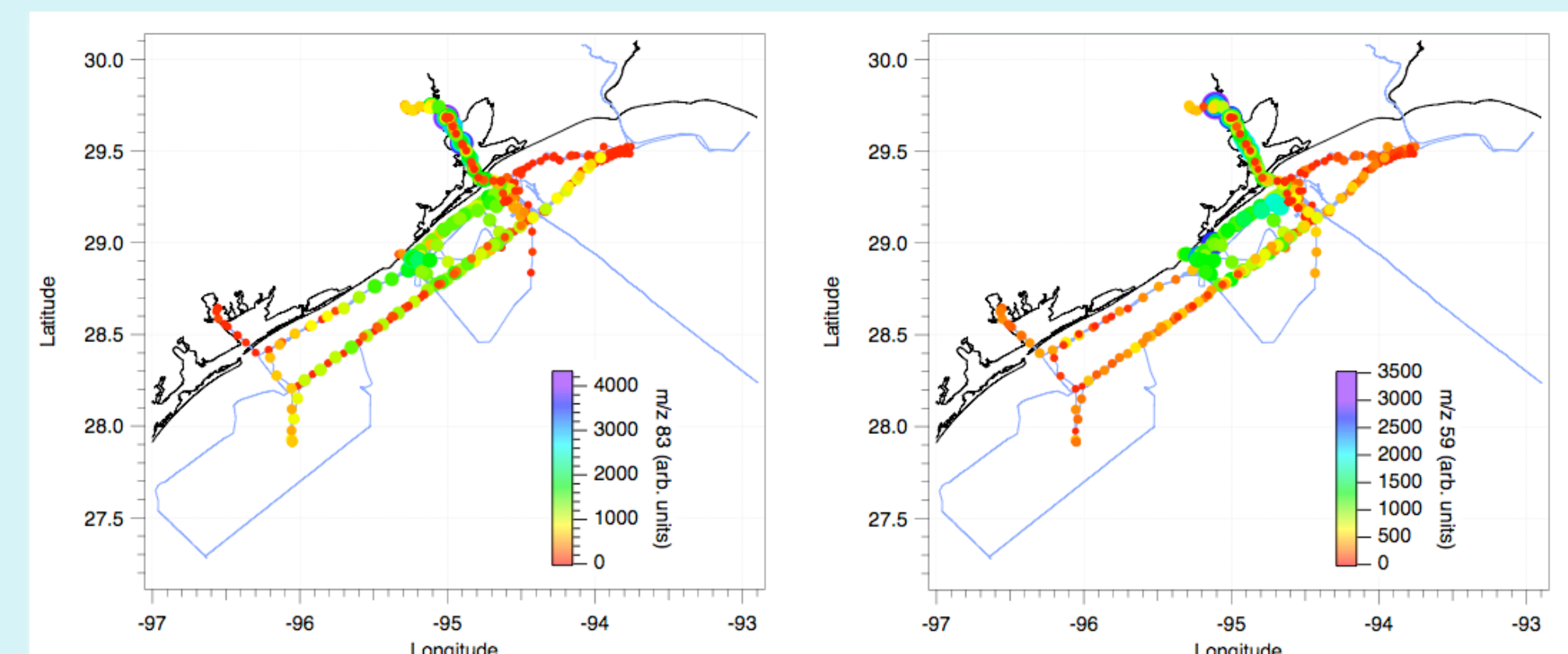


Figure 4: *Ronald H. Brown* cruise track showing locations of measurements colored by measured (left) $m/z\ 83$ signal and (right) $m/z\ 59$ signal.

992 valid ambient sample measurements were made between August 11 and September 11. Signals significantly detectable above the variation in instrumental background were observed at a number of mass/charge ratios, time series for 11 of which are shown in Figure 1. The signals shown are in units of integrated signal area (arbitrary) per desorption. Signals prior to August 30 were typically near or below detection limit while the estimated oxidized organic aerosol (OOA) mass (based on PMEL AMS measurements) in the 0.5 - $1.0\ \mu m$ size range averaged less than $0.25\ \mu g\ m^{-3}$ and flow was predominantly from the south and southeast (Gulf). Beginning August 30 and extending through September 9, significantly higher levels of OOA (average $1.23\ \mu g\ m^{-3}$) were encountered amid a general increase in products of photochemistry. Signals at most of the detected masses exhibited a broad increase during this time period (see Figure 3), although the shorter timescale structure differed among the masses, indicating varying composition of the aerosol organic fraction. This could indicate differences in the source VOCs responsible for the organic aerosol mass (SOA), or differences in the degree of photochemical processing of the aerosol-phase organic compounds. The two strongest signals measured were at $m/z\ 59$ and $m/z\ 83$. The compounds measured at these masses have not yet been determined, but $m/z\ 59$ would be the protonated molecular ion for glyoxal, a product of aromatic photooxidation that has been shown to partition into the aerosol phase. $m/z\ 83$ is possibly a fragment ion from carboxylic acids or di-acids, but additional laboratory work is needed to test this. The spatial distributions of the observed signals at $m/z\ 83$ and $m/z\ 59$ are shown in Figure 4 by plotting the locations of acquired samples along the ship cruise track and indicating the signal level by size and color of the marker. The two signals have similar, but not identical, spatial extent and the observed maxima occur in somewhat different locations (San Jacinto Point for $m/z\ 59$, mid-Galveston Bay for $m/z\ 83$). A more detailed time series of the variation of the $m/z\ 59$ and $m/z\ 83$ signals along with the estimated OOA and NO_2 (products of NO_x oxidation, $NO_x = NO_y - NO_y$) traces are shown in Figure 5. Several highlighted times show the differences in the temporal trends of the signals and variation of the composition even while the AM shows little change in the total OOA signal. Figure 6 shows plots of the correlations of $m/z\ 73$ (left) and $m/z\ 83$ (right) signals with the $m/z\ 59$ signal. Both show positive correlations with $m/z\ 59$, as would be expected if all are products of photochemical processing of VOCs. The correlation of $m/z\ 73$ with $m/z\ 59$ ($r = 0.79$) is closer than that of $m/z\ 83$ ($r = 0.70$), perhaps indicating a more similar formation path or set of precursor species. Figure 7 shows correlation plots of $m/z\ 83$ (left) and $m/z\ 59$ (right) signals with the corresponding signals from the gas-phase PIT-MS measurement. $m/z\ 83$ was almost never present in the gas phase (no correlation), while $m/z\ 59$ shows some correlation ($r = 0.51$) with the gas-phase acetone ($m/z\ 59$) measurement, as might be expected since acetone is a common product of VOC oxidation.

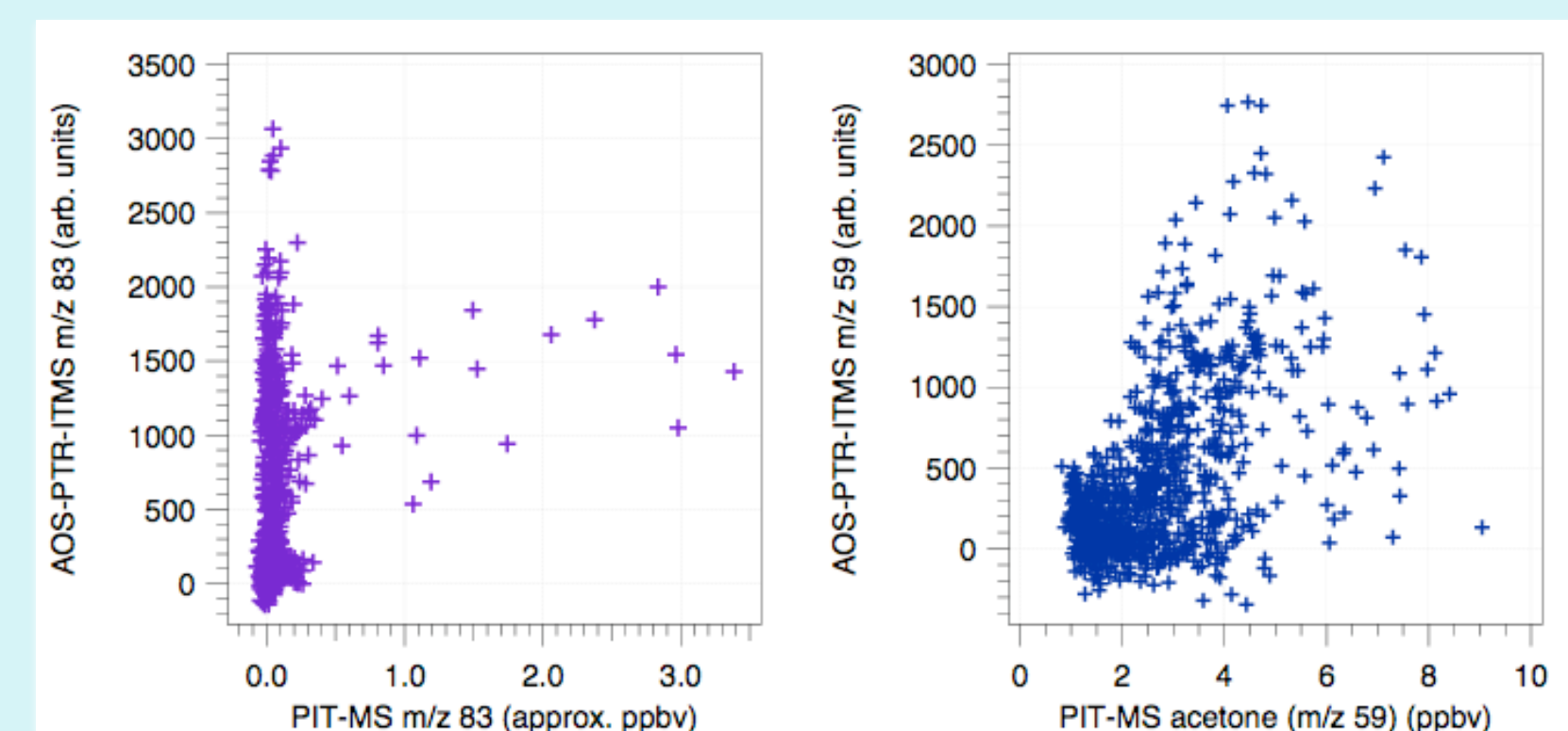


Figure 7: Observed relationship between aerosol and gas-phase signals at the mass

RESULTS II - Pyridine

Unlike the other mass signals measured by the AOS-PTR-ITMS during the 2006 TexAQs/GoMACCS cruise, $m/z\ 80$ did not show a broad enhancement during the extended photochemically active period near the end of mission (see Figure 3). Instead, $m/z\ 80$ was observed in relatively short duration events, typically less than 2 hours long, and near zero the rest of the time. These events were easily seen in the data since there was very little instrumental background at $m/z\ 80$. Plotting the measured $m/z\ 80$ signal on the ship's cruise track reveals that all of the elevated measurements occurred while the ship was on station in Barbour's Cut, with the exception of one event that occurred while we were docked at San Jacinto Point (Figure 8). A closer examination of the data taken in Barbour's Cut (Figure 9) shows that not all spectra acquired in Barbour's Cut had measureable $m/z\ 80$ signals, but those that did typically occurred when local winds were light and from a westerly direction (Figure 9) and between midnight and 9 am local time (CDT) (Figure 10, left). The largest events were measured between midnight and 5 am, most likely within a shallow nocturnal boundary layer. A protonated ion $m/z\ 80$ is an even mass indicates that the molecule ($mass = 79$ amu) most likely contains a nitrogen atom. Of the potential candidates at this mass, the most likely is pyridine (Figure 11). Pyridine is a common industrial solvent and is used in the synthesis of a variety of chemical products including pesticides and resins. Pyridine has a high proton affinity (222.3 kcal/mol) and would be easily ionized by PTR. Pyridine has a relatively high vapor pressure (~ 23 Torr @ $27^\circ C$) but is quite soluble and might partition between the gas and aerosol phases. Detecting pyridine in the gas phase with the PIT-MS instrument is complicated by the presence of a benzene isotope signal at the same m/z . The gas-phase pyridine signal was reconstructed by removing the benzene isotope signal at $m/z\ 80$ calculated from a regression of $m/z\ 80$ with $m/z\ 79$ (main benzene signal) during benzene spikes. The observed aerosol signal is plotted against this reconstructed gas-phase signal in Figure 10 (right). The plot is colored by time during the cruise and the individual events can be seen corresponding to those seen in the time-of-day plot (Figure 10, left). These results might indicate an episodic emission containing pyridine from one of the industrial complexes near Barbour's Cut.

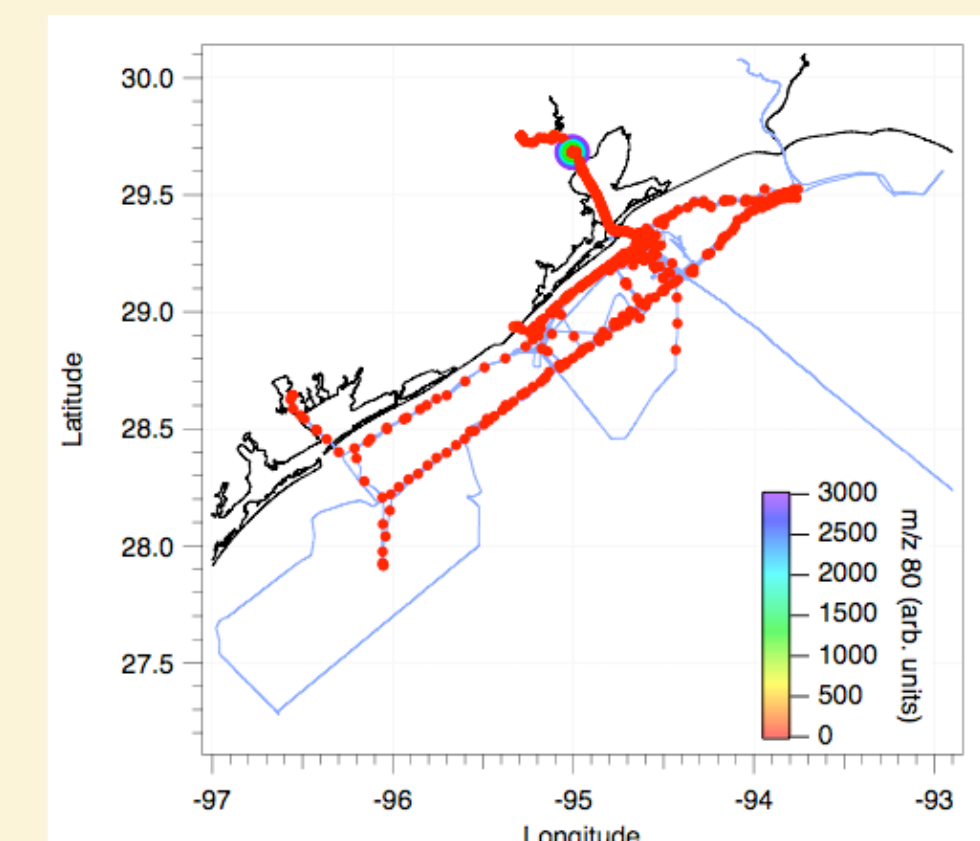


Figure 8: Ship course showing observed $m/z\ 80$ signals



Figure 9: View of Barbour's Cut showing observed elevated $m/z\ 80$ signals with local wind directions

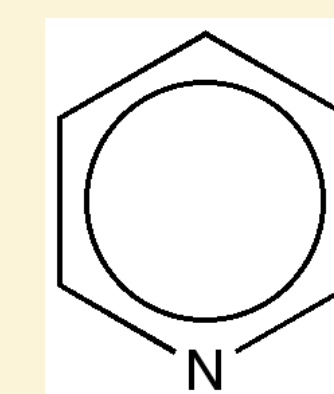


Figure 11: pyridine molecular structure.

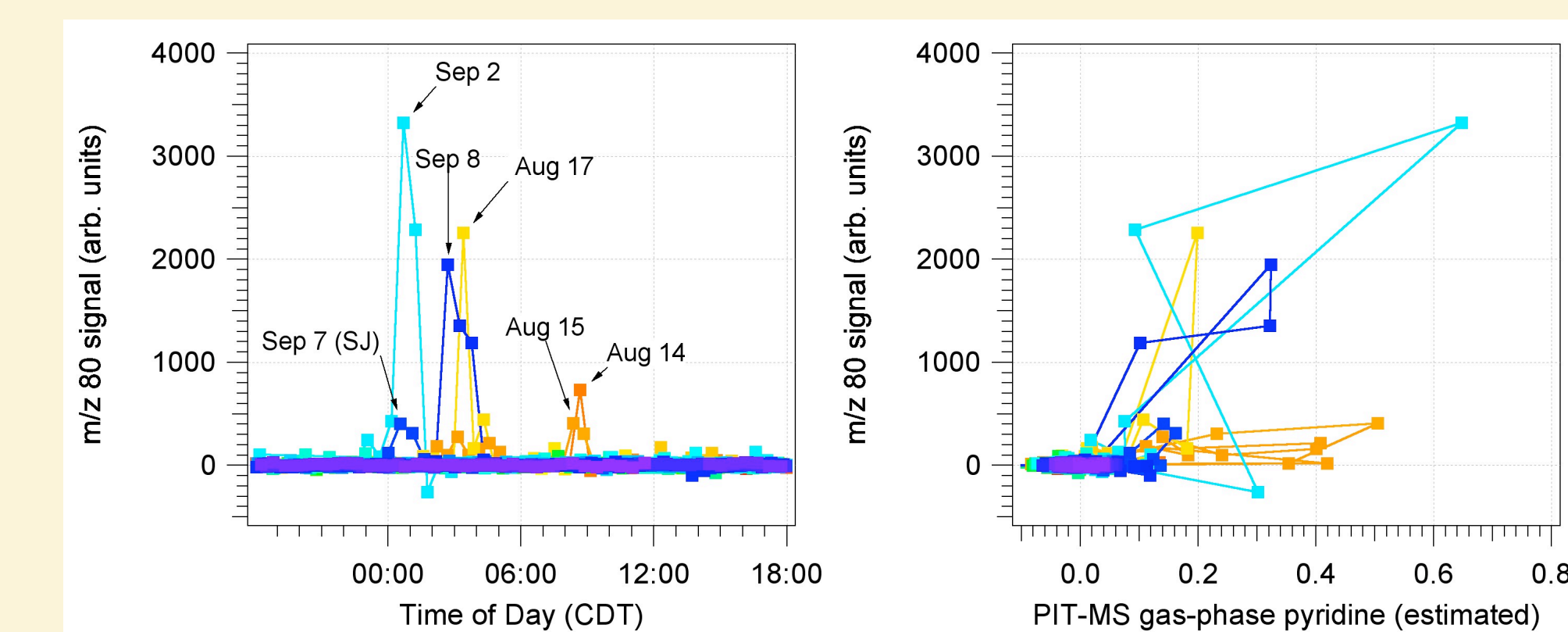


Figure 10: Plot of $m/z\ 80$ signal versus local (CDT) time of day (left) and the observed correlation between aerosol and gas-phase (after removing benzene isotope) signals (right).

Summary

- New aerosol organic PTR-ITMS instrument was fielded in a complex environment
- Detection limit for test aerosol organic: 10 - $20\ ng\ m^{-3}$
- Definite signals observed at a number of masses
- Different masses exhibited temporal/spatial variations
- Individual mass signals not always correlated with proxy for AMS total organic mass
- Compound identification complicated based on mass alone: glyoxal, methyl glyoxal, organic acids?
- Detection of aerosol phase pyridine and gas-particle partitioning?
- Working with other data for further comparison and analysis: AMS HOA vs. OOA, W-TOF AMS data, others